

AD-A184 277

TETRAHEDRAL CARBON AND INTERSTITIAL ELECTRONS IN LI
CLUSTER CLi_4 AND $(LiCH_3)_4(U)$ PENNSYLVANIA UNIV
PHILADELPHIA DEPT OF PHYSICS R P HESSNER ET AL JAN 87
TR-4 N00014-86-K-0304

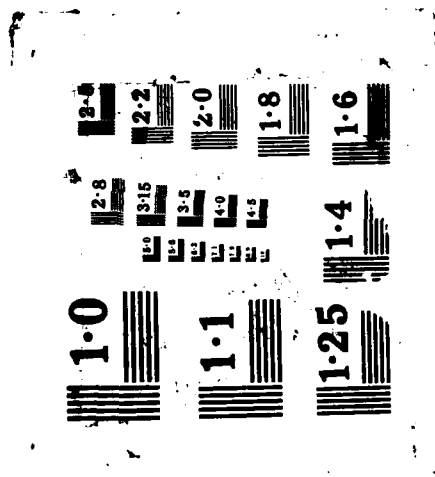
1/1

UNCLASSIFIED

F/G 7/2

NL





AD-A184 277

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0304

R&T Code 413F0005

Technical Report No. 4

DTIC
ELECTE
SEP 01 1987
S D
CLD

Tetrahedral Carbon and Interstitial Electrons in Li Cluster: CLi_4 and $(\text{LiCH}_3)_4$

by

Richard P. Messmer and R.C. Tatar

Prepared for Publication

in the

Journal of the American Chemical Society

University of Pennsylvania
Department of Physics
Philadelphia, PA

January 1987

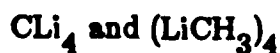
Reproduction in whole or in part is permitted for
any purpose of the United States Government

* This document has been approved for public release
and sale; its distribution is unlimited.

*This statement should also appear in Item 10 of the Document Control Data-DD
Form 1473. Copies of the form available from cognizant contract administrator.

87 9 1 010

Tetrahedral Carbon and Interstitial Electrons in Li Clusters:



R.P. Messmer*

General Electric Corporate Research and Development

Schenectady, NY 12301

and Department of Physics, University of Pennsylvania

Philadelphia, PA 19104

R.C. Tatar

Department of Physics, University of Pennsylvania

Philadelphia, PA 19104

The use of *ab initio* electronic structure calculations which include important electron correlation effects have yielded recently two quite significant findings.⁽¹⁻⁷⁾ The first, is the discovery by McAdon and Goddard¹ that bonding in alkali metal clusters and simple metals is *via* interstitial one-electron bonds. The second is that the carbon atom employs essentially tetrahedral hybrid orbitals not only for single bonds in saturated molecules, but also for double bonds,^(2,3) triple bonds^(4,5) and conjugated molecules such as benzene.⁽⁷⁾ The object of the present work is to illustrate how these two concepts about chemical bonding can be combined to provide a simple consistent physical picture of the bonding in CLi_4 and $(\text{LiCH}_3)_4$. The basic principles illustrated by these two molecules provide the basis for understanding the structure and bonding of a wide class of organolithium compounds.

There is chemical evidence⁸ for the existence of CLi_4 but the molecular structure does not appear to have been determined. However, *ab initio* calculations using the molecular orbital approximation have calculated the most stable

1230 /

structure to be tetrahedral in nature.^{9,10} On the basis of the results of previous generalized valence bond calculations,¹⁻⁷ one would anticipate the bonding in CLi_4 to be described in the following manner: (1) there will be four interstitial electrons, one localized in each of the four faces of a tetrahedron of Li atoms, (2) there will be a carbon atom at the center of the Li-tetrahedron which has four tetrahedrally-oriented hybrid orbitals each containing one electron and each pointing toward one of the faces of the tetrahedron, (3) an interstitial orbital and a carbon hybrid orbital mutually overlap to form a two-electron bond in each of the four tetrahedral faces. This description contrasts markedly with previous discussions of the bonding,⁸ yet it is the one we find via the generalized valence bond (GVB) calculations¹¹ described below.

The bonding in $(\text{LiCH}_3)_4$ should be similar to that of CLi_4 as far as the tetrahedron of Li atoms is concerned, however the species bonding to the interstitial electrons is no longer a single carbon atom forming four bonds from the interior of the Li cluster, but four methyl radicals bonding to the faces from the exterior of the cluster. Again, this simple physical picture is verified by the calculations presented below.

In Figure 1a, the geometry of the CLi_4 molecule is illustrated and a schematic representation of the orbitals describing one of the carbon-metal bonds is shown. Figure 1b shows a contour plot of one of the four equivalent bonding orbitals, ϕ_{1c}' , in the tetrahedral Li_4 cluster.¹² The electron described by this orbital is localized in the face containing Li atoms 1, 3 and 4. The orbital contour plots of Fig. 1c show the two orbitals of the bond in the face of the Li cluster, while Fig. 1d shows the same two orbitals in the plane containing Li atoms 1 and 2 and the carbon atom. The left panel of Fig. 1d should be compared to Fig. 1b — it shows the effect of the carbon atom on an interstitial electron in a face of the Li cluster. Because of its less screened nuclear charge, the carbon atom localizes the orbitals



✓

□

□

A-1

in the Li cluster faces to a greater extent than they are in the isolated metal cluster. This also facilitates better bonding between the metal and carbon. There are four equivalent bonds in CLi_4 , only one of which is illustrated in Figure 1.

The bonding in the $(\text{LiCH}_3)_4$ molecule can be understood by removing the interior carbon atom of Figure 1 and replacing it with four external methyl groups. The structure is shown schematically in Figure 2a where one set of the only unique types of bonds (C-H and C-Li cluster bonds) are highlighted. The contour plots in Figs. 2b and 2c are in the plane of the atoms H_1 , C_1 , Li_1 and Li_2 shown in Fig. 2a. In the contour plots of Fig. 2b, one can observe how orbital ϕ'_{1s} of the Li_4 cluster is modified by bonding to the free orbital of a methyl radical (ϕ'_{1s}). A C-H bond is illustrated by the contour plots of Fig. 2c; note the similarity of the C_1 orbitals ϕ'_{1s} and ϕ'_{2s} , one of which is bonded to the face of the Li cluster while the other is bonded to a hydrogen atom. The geometry for our calculations was taken from the solid state structure,¹³ and a double zeta basis set was used in the calculations.¹⁴

Previous calculations^{15,16} on $(\text{LiCH}_3)_4$, using localized molecular orbitals to discuss the bonding, have described the bonding as highly ionic in character¹⁵ and showing "essentially no metal-metal bonding".¹⁶ These descriptions contrast markedly with that obtained above. Furthermore, the differences between molecules containing carbon and hydrogen and those containing carbon and lithium is quite apparent and not very surprising.^{17,18} This contrasts with the view: "Surprisingly, when lithium is involved instead of hydrogen, the situation is completely different."¹⁹ In fact, the bonding picture which emerges from our work is close to the qualitative discussion given by Stucky and coworkers.²⁰

Acknowledgments. This work was supported in part by the Office of Naval Research. The authors are grateful to Dr. K.A. Smith for several useful discussions.

- [1] (a) McAdon, M.H.; Goddard III, W.A. *Phys. Rev. Lett.*, 1985, 55, 2563. (b) McAdon, M.H.; Goddard III, W.A. *J. Non-Cryst. Solids*, 1985, 75, 149.
- [2] Messmer, R.P.; Schultz, P.A.; Tatar, R.C.; Freund, H.-J. *Chem. Phys. Lett.*, 1986, 126, 176.
- [3] Palke, W.E. *J. Am. Chem. Soc.*, 1986, 108, 6543.
- [4] Messmer, R.P.; Schultz, P.A. *Phys. Rev. Lett.*, 1986, 57, 2653.
- [5] Messmer, R.P.; Schultz, P.A. *J. Am. Chem. Soc.*, 1986, 108, 7407.
- [6] Messmer, R.P. *Chem. Phys. Lett.*, 1986, 132, 161.
- [7] Schultz, P.A.; Messmer, R.P., submitted for publication in *Phys. Rev. Lett.*
- [8] Landro, F.J.; Gurak, J.A.; Chinn, J.W., Jr.; Lagow, R.J. *J. Organomet. Chem.*, 1983, 249, 1.
- [9] Collins, J.B.; Dill, J.D.; Jemmis, E.D.; Apeloig, Y.; Schleyer, P.v.R.; Seeger, R.; Pople, J.A. *J. Am. Chem. Soc.*, 1976, 98, 5419.
- [10] We adopt the calculated geometry of Ref. 8 as an expedient rather than calculating the optimal geometry using our correlated wave functions. Our interest here is in understanding the nature of the bonding rather than in determining accurate geometrical parameters for the molecule.
- [11] Bair, R.A.; Goddard, W.A., III; Voter, A.F.; Rappe, A.K.; Yaffee, L.G.; Bobrowicz, F.W.; Wadt, W.R.; Hay, P.J.; Hunt, W.J. GVB2P5 Program (unpublished). Bair, R.A.; Ph.D. Thesis, Caltech (1980). Hunt, W.J.; Hay, P.J.; Goddard, W.A., III, *J. Chem. Phys.*, 1972, 57, 738. Bobrowicz, F.W.; Goddard, W.A., III In "Modern Theoretical Chemistry"; Schaefer, H.F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4.

- [12] The calculations for the Li_4 cluster are for the quintet state as it is the most appropriate reference for discussing the two molecules considered here. Note that unlike covalently bonded systems, the high spin state of Li_4 is also bound. See ref. [1].
- [13] (a) Weiss, E.; Luchen, E.A.C. *J. Organomet. Chem.*, 1964, **2**, 197. (b) Weiss, E.; Hencken, G. *J. Organomet. Chem.*, 1979, **21**, 265.
- [14] Dunning, T.H., Jr.; Hay, P.J. In "Modern Theoretical Chemistry"; Schaefer, H.F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 1.
- [15] Guest, M.F.; Hillier, I.H.; Saunders, V.R. *J. Organomet. Chem.*, 1972, **44**, 59.
- [16] Graham, G.; Richtsmeier, S.; Dixon, D.A. *J. Am. Chem. Soc.*, 1980, **102**, 5759.
- [17] The ease with which Li forms hybrids from its s and p orbitals leads to properties vastly different from those of H. See refs. [1], [18] and [6].
- [18] Pauling, L. "The Nature of the Chemical Bond", 3rd Edition (Cornell University Press, NY, 1960), p. 431.
- [19] Schleyer, P.v.R.; Wurthwein, E.-U.; Kaufmann, E.; Clark, T.; Pople, J.A. *J. Am. Chem. Soc.*, 1983, **105**, 5930.
- [20] Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.*, 1974, **96**, 6048.

Figure Captions

Figure 1

(a) Schematic representation of the CLi_4 structure showing one of the four equivalent bonds. ϕ_{1s} is an interstitial electron in a face of the Li_4 tetrahedron; ϕ_{1s} is a hybrid orbital on carbon pointing into a face of the tetrahedron. These two orbitals overlap to form one of the four bonds.

(b) Contour plot of one of the interstitial orbitals (ϕ_{1s}') of the Li tetrahedron before the carbon atom is introduced.

(c) Contour plots of the two orbitals of (a), which form one of the carbon-metal bonds. Plots are in a triangular face of the Li tetrahedron.

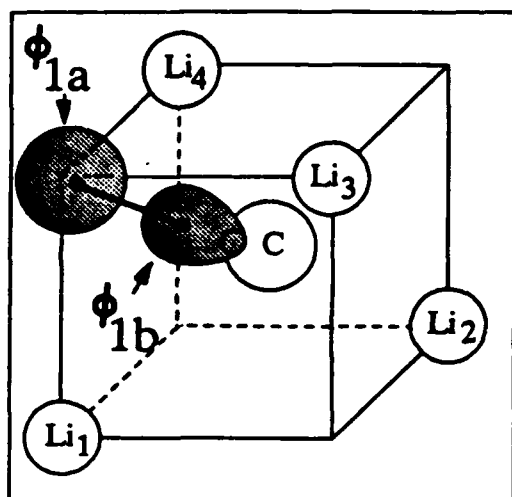
(d) Contour plots of the same two orbitals, but in the plane used in (b). The contours used in this Figure and in Figure 2 have the most diffuse contour as 0.025 au and the contours increment in steps of 0.025 au.

Figure 2

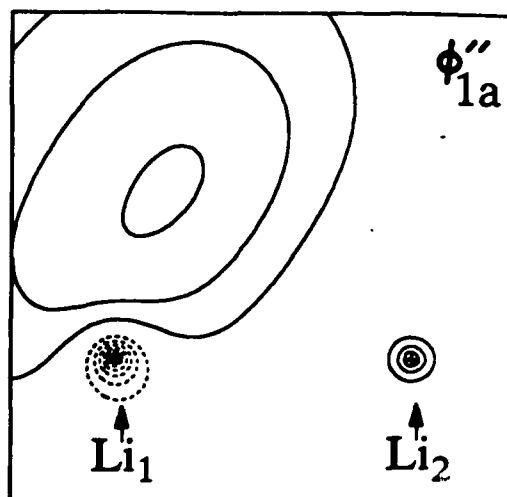
(a) Schematic representation of the LiCH_3 tetramer structure showing an example of the two types of bonds formed. ϕ_{1s}' and ϕ_{1s}' form a carbon-metal bond, while ϕ_{2s}' and ϕ_{2s}' form a carbon-hydrogen bond. The symbol "Me" shows the positions of the other methyl groups.

(b) Contour plots of the orbitals forming the carbon-metal bond in the plane containing atoms H_1 , C_1 , Li_1 and Li_2 .

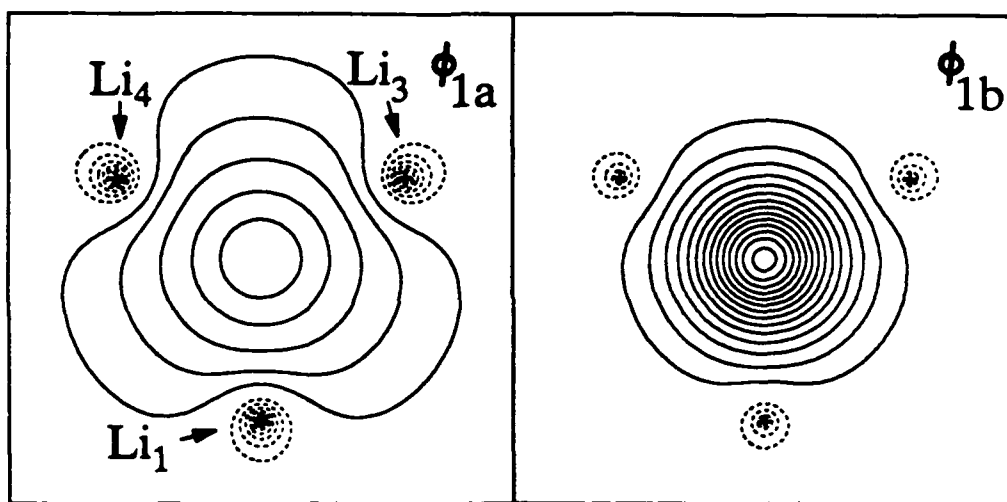
(c) Contour plots of the orbitals forming a carbon-hydrogen bond in the same plane as in (b).



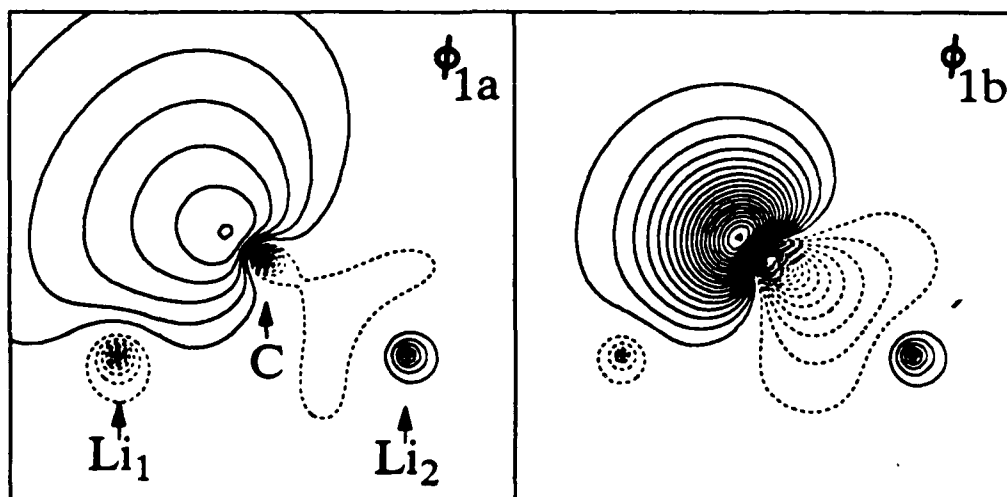
(a)



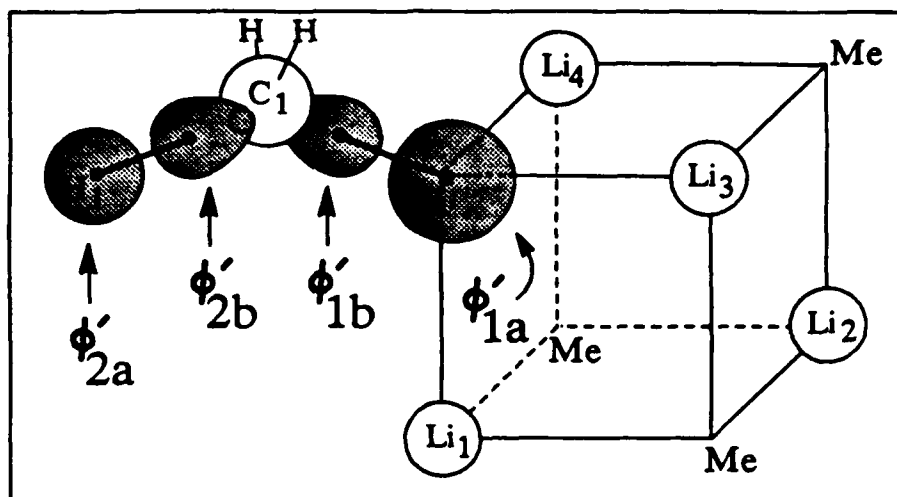
(b)



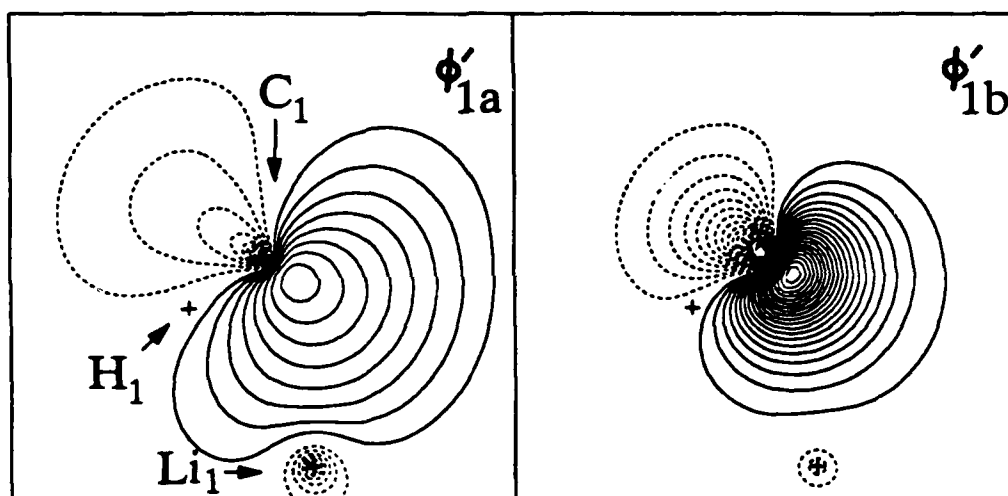
(c)



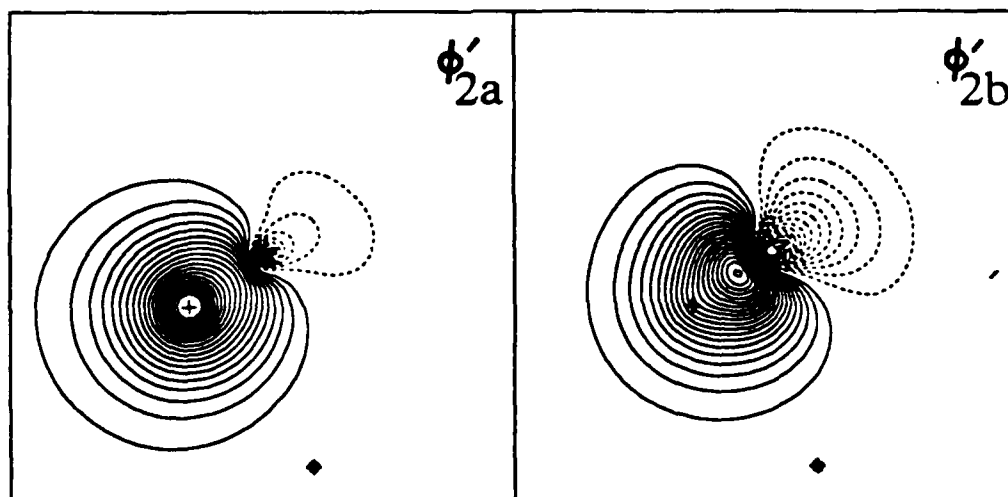
(d)



(a)



(b)



(c)

END

10-87

DTIC